tor response in terms of transmittance may be used for accurate determinations of oligomer concentrations has been confirmed experimentally. The validity of equation (5) has been verified with dilute chloroform solutions of bis(2-hydroxypropyl)terephthalate (*Figure 2*). Further, a linear relationship between the quantity of oligomer applied to the g.p.c. column and the corresponding chromatogram areas has been obtained (*Figure 3*).

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Photometric determination of gel point in PVC thermal degradation

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INTRODUCTION

In the thermal degradation of PVC in parallel with the primary process of allyl-activated dehydrochlorination, secondary reactions also take place[1–3]. One of them is crosslinking: as a consequence of this, even at an early stage of HCl elimination, the thermally degraded PVC becomes partly insoluble[4,5]. The crosslinking process can be characterized by the gel point, i.e., the first appearance of insoluble polymer in the course of degradation, an important parameter also from the practical point of view.

Table 1 Gel point of different PVC powder samples degraded at 180°C in argon atmosphere

	t_g (min)	
K	From gel fraction	Photometrically determined
38.3	240	245
49	250	248
62.6	114	116
69	310	310
79.5	181	183

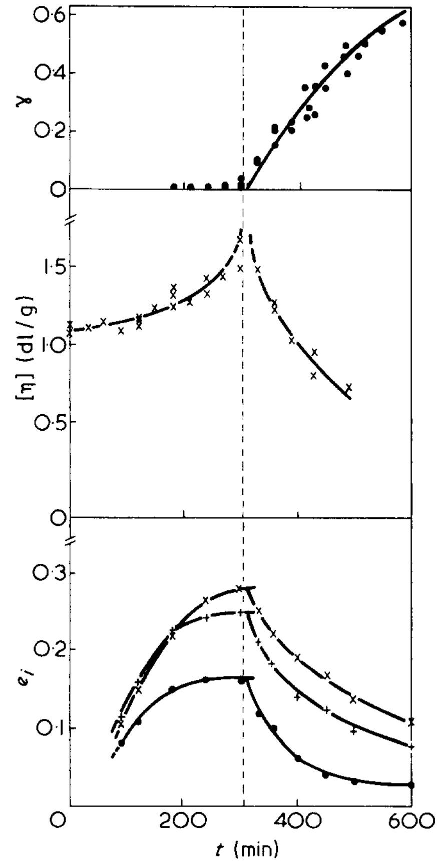

Figure 1 The specific absorbancy ($e_i = E_i/cd$, i = 5, 7, 10), the gel fraction (γ), and the intrinsic viscosity, [η], as a function of degradation time. (K = 69, 180°C, Ar; (— — —), gel point)

EXPERIMENTAL

PVC powder samples of different Fikentscher *K* values were degraded at 180°C in an argon atmosphere. The insoluble part of the treated samples was determined by gravimetry. Viscosity measurements were made at 25°C in cyclohexanone with an Ubbelohde viscometer. Solution spectra of degraded PVC in THF were registered on Specord UV–VIS spectrophotometer (Zeiss/Jena). Freshly distilled, peroxide-free THF was used.

Photometric determination of gel point

In the primary process of thermal PVC degradation hydrogen chloride splits off from the polymer backbone, producing conjugated unsaturated structures. The collective absorption of these polyenes gives a characteristic absorption spectrum, which may also be used for quantitative determination[2,6–12]. The maxima can be assigned to polyenes having different numbers of double bonds.

In studying the solution spectra of thermally degraded PVC powder samples, we have found that for the polyene with i double bonds the quantity

$$e_i = \frac{E_i}{cd} \qquad (1)$$

(i.e. the specific absorbance for unit concentration of PVC and unit path length) changes as a function of degradation time according to a kinked curve (E_i is the absorbancy, c is the concentration of polymer solution and d is the optical path length). The time corresponding to the inflexion point is practically independent of the wavelength, i.e., from the double-bond number of the polyene investigated. The decrease of specific absorbance of the solution is a consequence of gel formation as the non-soluble phase contains a continually increasing part of polyenes.

On the *Figure 1* the gel fraction (γ), the intrinsic viscosity, [η], and the specific absorbance for different i values (e_i) are plotted as a function of degradation time (t) for the same PVC sample. The time of discontinuous change is very nearly the same in all cases and corresponds to the gel point of the system.

The reliability of the photometric gel point determination described above may be improved by plotting the log e_i values as a function of degradation time, as in this case the curve after the gel point becomes nearly linear (*Figure 2*).

Table 1 shows gel point values determined by gravimetry and by the photometric method, respectively, for

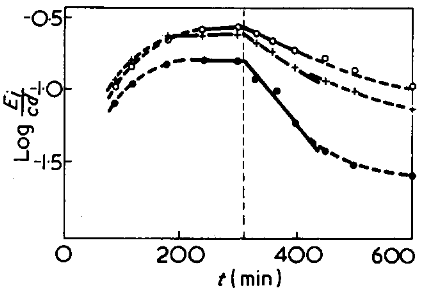

Figure 2 Logarithm of the specific absorbancy (log e_i) as a function of degradation time. (K = 69, 180°C, Ar; (– – –), gel point)

different PVC samples. In all cases essentially the same results were obtained by the different methods.

According to our experience, gel point values of the same reliability, as found by the gravimetric or viscometric method can be obtained by the photometric determination more quickly and with less effort.

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Electron spin resonance studies of spin-labelled polymers: 15. Spin probe measurements of plasticized poly(vinyl acetate)

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INTRODUCTION

The glass transition temperature, T_g, of an amorphous polymer is often associated with the β relaxation of mechanical and dielectric loss measurements. The transition is thus associated with the onset of main chain segmental motion and the result of any measurement of T_g will depend on the characteristic time of the experiment.

The spin probe technique is the most recent addition to methods for studying relaxations in amorphous polymers. The experiment involves the preparation of a dilute dispersion of a stable nitroxide radical in the relevant polymer and a study of the changes in shape of the electron spin resonance spectrum as a function of temperature. At low temperatures, the spectrum is dominated by the anisotropic coupling between the unpaired electron and the ^{14}N nucleus. Subtle changes in shape of the dispersion mode under varying conditions of microwave power and field modulation frequency enable correlation times τ as long as 10^{-5} sec to be measured[1]. In the region $10^{-9} < \tau < 10^{-7}$ sec there are well defined changes in the absorption mode, in particular the separation between the high- and low-field extrema decreases monotonically with τ[2–4]. It is expected that a marked change in shape will occur when

$$\tau^{-1} \sim \frac{4\pi}{3}\left[T_{zz} - \frac{1}{2}(T_{xx} + T_{yy})\right]$$

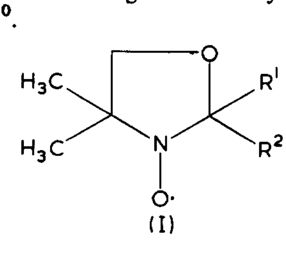
where the T's are the principal values of the hyperfine coupling tensor. Typical values for T_{xx}, T_{yy} and T_{zz} for dialkyl and saturated cyclic nitroxides lead to values for τ at this critical region of $\sim 3 \times 10^{-9}$ sec. For longer correlation times, the spectral shape is characteristic of the solid whilst at shorter times the typical motionally-narrowed spectrum is observed.

Following the early work of Rabold[5], Kumler and Boyer have made extensive use of an empirical parameter T_{50G} to characterize this transition region. This is the temperature at which the extrema separation is 50 gauss and a correlation has been established between T_g and T_{50G} for nineteen different polymers and copolymers using 2,2',6,6'-tetramethyl-4-hydroxypiperidin-1-oxyl benzoate as the paramagnetic probe[6]. Later work by these authors has included studies of the effect of probe size[7] and an investigation of the glass transition temperatures of some block copolymers[8].

Copolymers may be conveniently considered as polymer–diluent systems. Another important class of diluents are plasticizers and the purpose of this Note is to present a correlation between T_{50G} and the weight percentage of the polymer poly(vinyl acetate) (PVAc) plasticized with dimethyl- and diethylphthalates (DMP and DEP respectively).

EXPERIMENTAL

The probe used was 2,2',5,5'-tetramethyl-3-oxazolidinyloxy (TMOZ) (I, $R^1 = R^2 = CH_3$) and was prepared from acetone and 2-amino-2-methylpropan-1-ol using the Keana synthesis[9,10].



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